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(Unclassified Title)

**STUDIES OF STABILITY PROBLEMS
IN ADVANCED PROPELLANTS**

A. D. McElroy
J. W. Nebgen
Midwest Research Institute

Contract No. FO4611-67-C-0022

December 1967

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FOREWORD

This program has been conducted at Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri, 64110, under the general supervision of Mr. R. L. Hughes, Director, Chemistry Division. Mr. A. D. McElroy, Head, Physical and Inorganic Section, is project leader. Personnel contributing to the program are Dr. J. W. Nebgen, Dr. W. V. Beat, Mr. J. Caratena, and Mr. Glenn A. Chaplin. The program was monitored by 1/Lt. Ray Foscante, RPCS, Edwards Air Force Base.

The research covered by this report has been conducted under Contract No. FO4611-67-C-0022, AFSC Project No. 3148 (Midwest Research Institute Project No. 3006-C) and covers the period 1 October 1966 - 30 September 1967.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

This technical report has been reviewed and is approved.

W. H. EBELKE, Col., USAF
Chief, Propellant Division

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ABSTRACT

(C) The compatibility and stability characteristics of hydroxylammonium perchlorate (HAP) and hydrazinium dperchlorate (HP-2) have been studied. The inherent reactivities of the oxidizers with several types of organic substances were of particular interest. Both oxidizers are indicated by the study to be relatively weak oxidizers, with HP-2 being slightly more reactive than HAP. Both oxidizers, however, promote organic reactions of practical and fundamental interest. The latter reactions are those expected of organic substances in acid, dehydrating media.

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I.

INTRODUCTION

(C) Two advanced oxidizers, hydroxylammonium perchlorate (HAP) and hydrazinium diperchlorate (HP-2), are being evaluated by several organizations (Refs. 1 - 8) as candidate oxidizers in solid propellants. The performance potentials of both oxidizers are approximately equivalent, and superior to that of ammonium perchlorate. As might be expected, neither is as chemically inert or as inherently stable as ammonium perchlorate. It has been reported that HAP decomposes very slowly at 70°C (< 1 atm. in 7 months), and that HP-2 is less subject to decomposition (< 1 atm. in 18 months at 70°C). Propellant processing efforts have been relatively successful, though not without problems, and it thus is obvious that oxidizer-fuel compatibility does not pose a severe problem.

(C) Another advanced propellant ingredient of current interest is PBEP (Ref. 9) (poly bis-difluoroamino propylene oxide). PBEP is being evaluated (Refs. 10 and 11) as a prepolymer, primarily in urethane-based systems which necessarily must include an oxidizer such as HAP, HP-2, or ammonium perchlorate (AP). PBEP must of course be generally viewed as a potential fluorinating agent, as a source of hydrogen fluoride, and perhaps as a source of volatile NF compounds such as N_2F_4 or NF_3 . Successful use of PBEP depends both on its chemical inertness and on its inherent stability.

(C) The program discussed herein had the general objective of fundamentally defining the compatibility characteristics of the three advanced propellant ingredients. Some attention was also given to their inherent stability, primarily to obtain data which would allow us to differentiate between reactivity and instability. The approach consisted broadly of measurements of the extent and nature of oxidizer-organic substrate interactions, and oxidizer decomposition, at ambient temperatures, 60°C and 85°C. Tested organic substrates varied from the aliphatic hydrocarbon through substances containing appropriate functionalities such as C-O-C, C-OH, RNC=O, R_xNH_{3-x} , aziridines, epoxides and urethanes. Generally, the tested substances were fairly simple low molecular weight compounds. In only one or two instances were cured or curing binder systems tested.

(U) The general questions we endeavored to answer in the program are as follows:

(U) 1. What is the order of reactivity in oxidizer-aliphatic hydrocarbon systems? Under what conditions does hexane, for example, begin to be reactive with HAP and HP-2?

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(U) 2. Do specific functionalities, for example ether, amine and carbonyl, promote oxidizer-fuel reaction, and if so what is the nature of reaction?

(C) 3. What features of the oxidizers are significant from a reactivity standpoint? In HP-2, for example, does the second mole of perchloric acid function both as a strong acid and a strong oxidizing agent?

(U) 4. What is the nature of compatibility between the oxidizers and substances used generally as propellant ingredients?

(U) Studies of PBEP were initiated late in the program, so only a few results have been obtained. In a follow-through program* PBEP is being studied in greater detail, and studies of HAP and HP-2 are being continued.

(C) Techniques used in the program were infrared spectroscopy (gas phase and condensed phases), gas chromatography (for nitrogen, oxygen, carbon dioxide, nitrous oxide, methane, and ethylene) and NMR and EPR spectroscopies. Neither NMR nor EPR were particularly useful. Changes were apparently too small to be observable by NMR. With EPR, long-lived radicals were with few exceptions not observed, so EPR was useful chiefly in the negative sense.

(U) Early in the program it was found that periods of several weeks were necessary for appreciable reaction in many fuel-oxidizer systems. As a consequence, glass sealed-tube reactors were used in a majority of the experiments to eliminate the possibility of leaks developing in ground joint seals. Sealed-tube volumes were about 10 cc. Quantities of oxidizers varied from 50 mg. to 200 mg. Gaseous reactants were charged to pressures of 50 - 100 mm. Hg, and approximately 100 mg. of liquid fuels was employed.

* Contract No. FO4611-68-00011, Midwest Research Institute,
"Studies of Advanced Oxidizers."

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II.

DISCUSSION

A. Oxidizing Ability of HAP

(C) Data obtained in this program strongly support the conclusion that HAP has little tendency to oxidize relatively nonfunctional organic compounds. At ambient temperatures for periods of 5 months, diethyl ether, hexane, propyl acetate, and ethylene oxide did not react with HAP (Table 1, p. 7). nor did HAP decompose in the presence of these substances. (Ethylene oxide polymerized in the presence of HAP, but no further reaction was detected.) Other examples of apparently complete oxidative inertness at ambient temperatures are acetone - 45 days (other reactions do occur), and 1,4-diethoxybutane - 24 days (other reactions occur).

(C) At 60°C, resistance of these relatively simple substances to oxidation by HAP is still quite good, though we have little data at 5 months. At about 2 months, the following substances were not oxidized, though the evolution of trace (less than 0.01 moles:100 moles of oxidizer) quantities of N_2O occasionally occurred: ethanol, hexane, butene-1, isooctane, diethyl ether, ethyl acetate, propyl acetate, CS-15,* R45-M, ethylene glycol dimethyl ether and ethylene oxide. After 4 months at 60°, HAP and propyl acetate evolved less than 0.1 CO_2 :100 HAP, about the same quantity of N_2O was found, and essentially no oxygen or nitrogen was found.

(C) At 85°C, as evidenced by CO_2 formation, the oxidizing ability of HAP toward the relatively simple (functionally) organic materials begins to be apparent. Even at 85° the oxidation is slight, as evidenced by evolution of less than 0.1 CO_2 :100 HAP from isooctane, ethylene glycol dimethyl ether, and MRPX after 1-1/2 to 2-1/2 months. Worthy of note is the fact that no CO_2 was detected over HAP plus diethyl ether after 64 days at 85°, even though nitrogen and N_2O were evolved in quantities approaching 1 mole per 100 moles of HAP; in addition, the ether was extensively dehydrated to ethylene.

(C) To summarize, we have found HAP to be stable in the oxidizing sense toward aliphatic hydrocarbons, ethers, alcohol, olefins, and esters at temperatures as high as 60° for periods of 2 months. At ambient temperatures, this lack of reactivity has been observed up to 5 months. At 85°C, the oxidizing power of HAP toward the above simple organic substances begins to be evidenced; even after two months, however, the extent of oxidation is still relatively slight. Furthermore, these substances do

* See Glossary of Terms, Appendix, p. 31.

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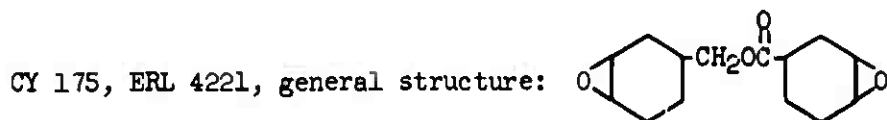
not promote the decomposition of HAP at ambient temperatures and at 60°C. At 85°C, HAP alone is subject to decomposition; surprisingly, the amounts of N₂O and nitrogen evolved from HAP plus simple organics are less than are evolved from HAP by itself. This fact suggests that the organic substances stabilize HAP, possibly by inhibiting volatilization of the oxidizer.

(C) In the above discussion it has been indicated that alkanes, aliphatic olefins, aliphatic ethers, esters, and alcohols are quite resistant to oxidation by HAP. This restriction implies that other functionalities are susceptible to oxidation. This we have indeed found to be the case, though in many instances it is doubtful that oxidation products, notably CO₂, truly arise by oxidation.

(C) Commercial epoxides usually evolve small amounts of carbon dioxide on contact with HAP after 1 - 2 months at 60°C, and occasionally at ambient temperatures. The quantities are small (always less than 1 mole:100 moles HAP), but the contrast between ethylene oxide and the commercial epoxides is nevertheless striking. ERL 0510 is, from our experience, the most compatible of the commercial epoxides. ERL 0500, the undistilled precursor of ERL-0510, is substantially less compatible than ERL 0510. This latter fact leads us to suspect that purity may be quite important with the commercial epoxides, a suspicion bolstered by the observations that ethylene oxide is oxidatively stable toward HAP, and that 1,2-epoxy-3-isopropoxy propane is nearly as unreactive as ethylene oxide.

(C) The epoxides universally polymerized in the presence of HAP, but the polymerization process is not believed to be a contributor to the relatively small amounts of oxidation. We would like to be able to pick a basic epoxide structure or a specific commercial epoxide as preferred candidates in propellant formulations. Such a selection is not justified by our data, for the following reasons: (1) We believe purity is perhaps as important as structure; and (2) Times required for measurable reaction are substantially longer than the lifetimes of the epoxide functionality in a curing propellant. The qualitative increasing order of reactivity is

(U) ERL 0510, trifunctional epoxide derived from N-N-triglyceryl-4-amino phenol



DER 732, DER 736: epoxy terminated polyethers.

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(C) One other feature of HAP-commercial epoxide reactions is worthy of note. Oxygen was almost universally evolved in small quantities (0.01 to 0.1 moles:100 moles HAP), and the quantity of oxygen was roughly proportional to the quantity of carbon dioxide. One concludes therefore that the epoxide-HAP reaction without question involves the ClO_4 group.

(U) Acetone and acetic acid must, based on limited data, be classified as slightly oxidizable by HAP at 60° . Acetone is subject to reactions which convert it largely to a slightly volatile liquid, possibly via aldol type condensations.

(C) Compatibility with N-H bearing systems varied roughly in proportion to the base strength of the amine. NTEB, an N(Raziridine)_3 aziridine, diluted with mineral oil was fairly reactive with HAP, generating nearly 1 CO_2 , more than 1 N_2O , and 12 N_2 :100 HAP in 25 days at 60°C . Under the same conditions MAPO, a $(\text{Raziridine})_3$ PO aziridine, in mineral oil generated no N_2O , less than 0.1 CO_2 :100 HAP, and 0.4 N_2 :100 HAP. HAP and MAPS (neat) were apparently compatible for 1 month at room temperature. HAP and polyetherdiamine L-2000 evolved some CO_2 ($< 0.1 \text{ CO}_2$:100 HAP), and close to 1 N_2O :100 HAP after 1 month at 60°C ; nitrous oxide also evolved at ambient temperatures. From these results one concludes that the weakly basic aziridine group is at best only slightly reactive with HAP. Stronger bases promote decomposition of HAP and enhance its oxidizing ability. The ability of amines to enhance decomposition of HAP is considerably more significant than the accompanying slight increase in oxidizing potential.

(C) Urethanes are apparently oxidized, as carbon dioxide slowly evolved from all urethanes tested. These consisted of ethyl-N-ethyl carbamate; ethyl-N-ethyl carbanilide; Adiprene L-100; a urethane prepared from R-45 M and $\text{C}_6\text{H}_5\text{NCO}$ (mol. wt. ca. 2400); and a urethane prepared from $\text{C}_6\text{H}_5\text{NCO}$ and a hydroxy terminated polypropylene oxide (urethane molecular weight ca. 900). The polypropylene oxide based urethane appears to be the most compatible (less than 0.1 CO_2 :100 HAP after 1 month at ambient temperatures). After 2 months at ambient temperatures, the carbon dioxide evolved from HAP plus ethyl-N-ethyl carbamate and ethyl-N-ethyl carbanilide approached 1 CO_2 :100 HAP. The R45 M based urethane performed similarly to the simple urethanes at ambient temperatures and at 60°C ; at 60°C the amount of evolved carbon dioxide was greater than 1 CO_2 :100 HAP after about 1 month. Adiprene L-100 was the most reactive urethane; its reactivity is in fact more typical of an isocyanate, which it is (see below).

(C) The mechanism of evolution of CO_2 from urethanes is an important question. The relatively higher order of compatibility found for the simple organic substances would indicate that HAP should not attack the aliphatic portions of tested urethanes. One is led to the conclusion that the point

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of attack is the RNHCOOR functionality, and that CO_2 evolves by decarboxylation rather than oxidation. We have attempted to clarify this point by NMR studies of reacting systems, by infrared examinations of residues, and by analyses of residues. None of these techniques were able to cope with the problem that changes affected only a small fraction (ca. 1%) of the reactants. Until evidence to the contrary is obtained, we are much inclined to view CO_2 evolution as a phenomenon resulting from acid catalyzed decarboxylation, with an assist from trace water.

(C) At this point we must say that CO_2 has been universally evolved, slowly, from the tested HAP-urethane systems. Included in the study were urethanes of molecular weights as high as 2400. Under ambient conditions the quantity of evolved CO_2 has been of the order of 0.1 to 1 CO_2 :100 HAP in a 2-month period. If trace water is indeed contributing to an acid-catalyzed decarboxylation, little more CO_2 may evolve in longer periods of time. This point will be studied in future research, as well as the effect of added proton-bearing substances.

(C) Data on isocyanates is somewhat scanty, due to the fact that this class of compounds was generally found to have a fairly high order of reactivity with HAP and with HP-2. Carbon dioxide is the major observed product at ambient temperatures and at 60° from HAP plus TDI, hexamethylenediisocyanate, and Adiprene L-100. Of these HMDI is by far the most reactive, and TDI the least. Though the data are a bit scarce to draw a definite conclusion, it appears that one should expect as a minimum about 1 CO_2 :100 HAP in 30 days at ambient temperatures. One concludes also that an aliphatic isocyanate is much less desirable than an aromatic isocyanate.

B. The Oxidizing Ability of HP-2

(C) Since one of its perchloric acid molecules titrates as a strong acid in water, and since HP-2 is susceptible to dissociation at elevated temperatures, one might expect this oxidizer to be a slightly more potent oxidizer than HAP. This we would have generally found to be true, though the conclusion became obvious only through a slowly developing pattern, a pattern which indicated that HP-2 definitely gave positive tests when HAP failed to give a positive test.

(U) Sixty experiments listed in Table 1 involving HAP (34 experiments) and HP-2 (26 experiments) plus ethylene oxide, ethylene glycol dimethyl ether, hexane, isooctane, butene-1, ethyl acetate, propyl acetate, acetone, propane, 1,4-diethoxybutane and 1,2-epoxy-3-isopropoxy propane were compared.

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TABLE 1

(C) STUDIES OF HAP AND HP-2

| Oxidizer-Fuel-°C-Days | Evolved Gases, Moles:100 Moles of Oxidizer | | | | | | | | | |
|--|--|------|----|----|----------------|----------------------|------------------|------|----|----|
| | CO ₂ | | | | O ₂ | N ₂ | N ₂ O | | | |
| | 0 | <0.1 | <1 | >1 | | | 0 | <0.1 | <1 | >1 |
| HAP-ethylene oxide-R.T.-126 | x | | | | 0 | 0 | x | | | |
| HAP-ethylene oxide-60°-37 | x | | | | | | x | | | |
| HP-2-ethylene oxide-60°-20 | | x | | | | 0.15xs ^{a/} | | | | |
| HP-2-ethylene oxide-60°-70 | | | x | | 0.75xs | 0.75 | | | | |
| HP-2-ethylene oxide-85°-20 | | | | x | 13xs | 8 | | | | |
| HP-2-ethylene oxide-R.T.-15 | x | | | | 0 | 0.30 xs | x | | | |
| HAP-1,2 epoxy-3-isopropoxypropane- R.T.-70 | x | | | | 0.01 | 0.02 | x | | | |
| HAP-1,2 epoxy-3-isopropoxypropane- 60°-51 | | | x | | 0.04 | 0.06 | x | | | |
| HP-2-1,2 epoxy-3-isopropoxypropane- R.T.-67 | x | | | | 0.03 | 0.12 | | | | |
| HP-2-1,2 epoxy-3-isopropoxypropane- 60°-46 and 51 | | x | | | 0.2xs | 0.15 | | | | |
| HP-2-ERL 0510-R.T.-105 | x | | | | 0 | 0 | | | | |
| HP-2-ERL 0510-60°-57 | x | | | | 0 | 0 | | | | |
| HAP-ERL 0510-R.T.-105 | x | | | | 0.15 | 1.0xs | x | | | |
| HAP-ERL 0510-60°-58 | | x | | | 0.3 | 0.8 | | x | | |
| HAP-ERL 4221-60°-24 | x | | | | | | x | | | |
| HAP-DER 732-R.T.-37 | x | | | | 0.01xs | | x | | | |
| HAP-CY 175-R.T.-41 | x | | | | 0.01 xs | | x | | | |
| HP-2-DER 736-R.T.-41 | x | | | | | | | | | |
| HP-2-DER 732-R.T.-36 | x | | | | 0.02xs | | | | | |
| HP-2-CY 175-R.T.-46 | x | | | | | | | | | |
| HAP-CY 175-60°-16 | | x | | | | | x | | | |
| HAP-CY 175-60°-36 | | x | | | 0.02xs | | x | | | |
| HAP-CY 175-60°-45 | | x | | | 0.06xs | | x | | | |
| HAP-ERL 4221-60°-44 | | x | | | 0.02xs | | x | | | |
| HAP-DER 736-R.T.-41 | | x | | | 0.03xs | | x | | | |
| HAP-ERL 4221-R.T.-36 | | x | | | 0.05xs | | x | | | |

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TABLE 1 (Continued)

| Oxidizer-Fuel-°C-Days | Evolved Gases, Moles:100 Moles of Oxidizer | | | | | | | | | |
|-----------------------|--|------|----|----|----------------|----------------|------------------|------|----|----|
| | CO ₂ | | | | O ₂ | N ₂ | N ₂ O | | | |
| | 0 | <0.1 | <1 | >1 | | | 0 | <0.1 | <1 | >1 |
| HP-2-CY 175-60°-14 | | x | | | 0.02xs | | | | | |
| HP-2-CY 175-60°-22 | | x | | | 0.02xs | | | | | |
| HP-2-DER 736-60°-9 | | x | | | | | | | | |
| HP-2-DER 732-60°-4 | | x | | | | | | | | |
| HAP-DER 736-60°-9 | | | x | | 0.10xs | | x | | | |
| HAP-DER 736-60°-28 | | | x | | 0.19xs | | x | | | |
| HAP-DER 732-60°-33 | | | x | | 0.12xs | | x | | | |
| HP-2-DER 736-60°-11 | | | x | | | | | | | |
| HP-2-DER 736-60°-19 | | | x | | 0.15xs | | | | | |
| HP-2-ERL 4221-60°-23 | | | x | | 0.07xs | | | | | |
| HAP-ethanol-60°-80 | x | | | | 0.02xs | | | | | x |
| HAP-ethanol-60°-20 | x | | | | | | | x | | |
| HAP-ethanol-60°-43 | x | | | | 0.02xs | | | | | x |
| HP-2-ethanol-60°-40 | x | | | | | | | | | |
| HP-2-ethanol-60°-70 | x | | | | 0 | 0.08xs | | | | |
| HP-2-R45M-60°-52 | x | | | | 0.1xs | 0.05 | | | | |
| HP-2-CS-15-60°-51 | x | | | | 0 | 0 | | | | |
| HAP-R-45M-60°-52 | x | | | | 0.1 | 0.2 | x | | | |
| HAP-CS-15-60°-50 | x | | | | 0.4 | 1.6 | x | | | |
| HAP-hexane-R.T.-148 | x | | | | 0 | 0 | x | | | |
| HAP-hexane-60°-56 | x | | | | | | x | | | |
| HAP-butene-1-60°-39 | x | | | | 0 | 0 | x | | | |
| HAP-propane-60°-26 | x | | | | | | | x | | |
| HP-2-propane-60°-70 | x | | | | 0 | 0.10xs | | | | |
| HAP-1sooctane-60°-76 | x | | | | 0.02 | 0.04 | x | | | |
| HAP-1sooctane-60°-83 | x | | | | 0 | 0.3xs | | | | |
| HAP-1sooctane-85°-38 | | x | | | 0.04xs | 0.05 | | | | x |
| HAP-1sooctane-85°-73 | | x | | | 0.02xs | | | x | | |
| HP-2-propene-85°-40 | | x | | | 0.05 | 2xs | | | | |

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TABLE 1 (Continued)

| Oxidizer-Fuel-°C-Days | Evolved Gases, Moles:100 Moles of Oxidizer | | | | | | | | | |
|--|--|------|----|----|----------------|----------------|------------------|------|----|----|
| | CO ₂ | | | | O ₂ | N ₂ | N ₂ O | | | |
| | 0 | <0.1 | <1 | >1 | | | 0 | <0.1 | <1 | >1 |
| HP-2-propane-60°-80 | | x | | | | 0.20xs | | | | |
| HP-2-hexane-R.T.-154 | | x | | | 0 | 0 | | | | |
| HP-2-hexane-60°-55 | | x | | | 0.03 | 0.60xs | | | | |
| HP-2-butene-1-R.T.-125 | x | | | | | | | | | |
| HP-2-butene-1-60°-39 | | x | | | | 0.06xs | | | | |
| HP-2-butene-1-60°-65 | x | | | | 0.02 | 0.1 | | | | |
| HP-2-isooctane-R.T.-140 | x | | | | 0.03 | 0.15 | | | | |
| HP-2-isooctane-60°-60 | | x | | | 0.01 | 0.70xs | | | | |
| HP-2-isooctane-85°-54 | | | x | | 0.60 | 20xs | | | | |
| HAP-MRPX-85°-42 | | x | | | 0 | 0 | | x | | |
| HAP-ethyl ether-85°-64 | x | | | | 0.01 | 0.6xs | | | | x |
| HAP-diethyl ether-85°-65 | x | | | | | 0.25xs | | | | x |
| HAP-diethyl ether-60°-34 | x | | | | | | | x | | |
| HAP-diethyl ether-60°-51 | x | | | | | | | x | | |
| HAP-ethyl ether-60°-141 | x | | | | 0 | 0 | x | | | |
| HAP-ethylene glycol dimethyl ether-60°-62 | x | | | | 0.01 | 0.02 | x | | | |
| HAP-ethylene glycol dimethyl ether-85°-40 | | x | | | 0.2xs | 0.06 | | x | | |
| HAP-ethylene glycol dimethyl ether-85°-68 | | x | | | 0.6xs | 0.01 | | | | x |
| HP-2-ethylene glycol dimethyl ether-60°-63 | | | x | | 0.25xs | 0.2 | | | | |
| HP-2-ethylene glycol dimethyl ether-85°-53 | | | | x | 5xs | 0.7 | | | | |
| HP-2-1,4 diethoxybutane-R.T.-19 and 22 | x | | | | 0 | 0 | | | | |
| HAP-1,4 diethoxybutane-R.T.-18 | x | | | | 0 | 0 | x | | | |
| HP-2-1,4 diethoxybutane-R.T.-22 | x | | | | 0.02 | 0.06 | | | | |
| HP-2-1,4 diethoxybutane-60°-18 | | x | | | 0.04 | 0.15 | | | | |
| HAP-1,4 diethoxybutane-R.T.-24 | x | | | | 0.01 | 0.03 | x | | | |
| HAP-1,4 diethoxybutane-60°-22 | | x | | | 0.02 | 0.06 | x | | | |
| HAP-ethyl acetate-60°-77 | x | | | | 0.01xs | | | x | | |

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TABLE 1 (Continued)

| Oxidizer-Fuel-°C-Days | Evolved Gases, Moles:100 Moles of Oxidizer | | | | | | | | | |
|--|--|------|----|----|--------------------|----------------|------------------|------|----|----|
| | CO ₂ | | | | O ₂ | N ₂ | N ₂ O | | | |
| | 0 | <0.1 | <1 | >1 | | | 0 | <0.1 | <1 | >1 |
| HAP-ethyl acetate-60°-26 | x | | | | 0.01xs | | | x | | |
| HP-2-ethyl acetate-60°-64 | | x | | | 0.02 | 0.08 | | | | |
| HAP-propyl acetate-R.T.-147 | x | | | | 0 | 0 | x | | | |
| HAP-propyl acetate-60°-55 | x | | | | | | | x | | |
| HAP-propyl acetate-60°-121 | | x | | | 0 | 0 | | x | | |
| HP-2-propyl acetate-60°-55 | | | x | | 0.08 | 1xs | | | | |
| HAP-acetic acid-60°-28 | | x | | | 0.01xs | | | | | |
| HP-2-acetic acid-R.T.-40 | | x | | | | | | | | |
| HP-2-acetic acid-60°-31 | | | x | | 0.03 | 0.25xs | | | | |
| HAP-Telagen CT-R.T.-111 | | | x | | 0.02 | 0.06 | x | | | |
| HP-2-Telagen CT-R.T.-111 | | | x | | 0.02 | 0.05 | | | | |
| HAP-Telagen CT-60°-54 | | | x | | 0.02xs | 0.01 | x | | | |
| HP-2-Telagen CT-60°-47 | | | x | | 0.02 | 0.06 | | | | |
| HAP-acetone-60°-28 | x | | | | 0 | 0 | x | | | |
| HAP-acetone-60°-51 | | x | | | 0 | 0 | | x | | |
| HAP-acetone-R.T.-45 | x | | | | 0 | 0 | x | | | |
| HP-2-acetone-R.T.-45 | x | | | | | | | | | |
| HP-2-acetone-60°-28 | | | x | | | | | | | |
| HAP-MAPS-R.T.-33 | x? | | | | N.D. ^{2/} | N.D. | x | | | |
| HP-2-MAPS-R.T.-34 | x? | | | | N.D. | N.D. | | | | |
| HP-2-NTEB-MRPX-60°-27 | x | | | | | | | | | |
| HP-2-MAPO-MRPX-60°-27 | x | | | | | | | | | |
| HAP-NTEB-MRPX-60°-25 | | | . | | 0 | 12xa | | | | x |
| HAP-MAPO-MRPX-60°-25 | | x | | | 0 | 0.40xa | | x | | |
| HAP-(urethane from ϕ NCO and HO terminated polypropylene oxide, M.W. = ~ 900)-R.T.-21 | | x | | | | | | | | |
| HAP-(urethane from ϕ NCO and HO terminated polypropylene oxide, M.W. = ~ 900)-60°-32 | | | | x | | | | | | |
| (urethane from ϕ NCO and HO terminated polypropylene oxide, M.W. = ~ 900)-R.T.-30 | x | | | | 0.003 | 0.01 | | | | |

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TABLE 1 (Continued)

| Oxidizer-Fuel-C-Days | Evolved Gases, Moles:100 Moles of Oxidizer | | | | | | | | | |
|--|--|------|-------|-------|----------------|----------------|------------------|------|----|----|
| | CO ₂ | | | | O ₂ | N ₂ | N ₂ O | | | |
| | 0 | <0.1 | <1 | >1 | | | 0 | <0.1 | <1 | >1 |
| (urethane from ϕ NCO and HO terminated polypropylene oxide, M.W. = ~ 900)-R.T.-21 | x | | | | 0.1 | 0.2 | | | x | |
| HAP-(urethane from ϕ NCO + R-45-M, M.W. = ~ 2500)-60°-49 | | | x | | 0 | 0 | x | | | |
| HAP-(urethane from ϕ NCO + R-45-M, M.W. = ~ 2500)-R.T.-35 | | | x | | | | x | | | |
| HAP-(urethane from ϕ NCO + R-45-M, M.W. = ~ 2500)-R.T.-8 | | x | | | 0 | 0 | x | | | |
| HP-2-(urethane from ϕ NCO + R-45-M, N.W. = ~ 2500)-R.T.-45 | | | x | | 0 | 0.05 | | | | |
| HP-2-(urethane from ϕ NCO + R-45-M, M.W. = ~ 2500)-60°-52 | | | | x | 0 | 0 | | | | |
| HAP-ethyl-N-ethyl carbamate-R.T.-60 | | | x | | 0 | 0 | | x | | |
| HAP-ethyl-N-ethyl carbanilide-R.T.-60 | | | x | | | | | | x | |
| HAP-ethyl-N-ethyl carbanilide-60°-22 | | | x | | 0 | 0.10xs | | x | | |
| HAP-ethyl-N-ethyl carbamate-60°-43 | | | | x | | 30xs | | | | x |
| HP-2-ethyl-N-ethyl carbanilide-60°-43 | | | | x | | | | | | |
| HP-2-ethyl-N-ethyl carbamate-R.T.-48 | | | | x | | | | | | |
| HP-2-ethyl-N-ethyl carbamate-60°-34 | | | | x | | | | | | |
| HAP-Adiprene L-100-R.T.-10 | | | | x | N.D. | N.D. | x | | | |
| HAP-Adiprene L-100-R.T.-28 | | | | x | | | | x | | |
| HAP-Adiprene L-100-60°-28 | | | | x | 0.01 | 0.20xs | x | | | |
| HP-2-Adiprene L-100-R.T.-5 | | | | x | N.D. | N.D. | | | | |
| HP-2-Adiprene L-100-R.T.-27 | | | | x | 0.05xs | 0.01 | | | | |
| HP-2-Adiprene L-100-60°-7 | | | | x | 0.10xs | 0.10 | | | | |
| HAP-TDI-60°-33 | | | | x | | | | | | x |
| HAP-HMDI-R.T.-15 | | | | x | N.D. | N.D. | | N.D. | | |
| HP-2-TDI-R.T.-46 | | | | x | 0.06 | 0.12 | | | | |
| HP-2-TDI-60°-7 | | | | x | | | | | | |
| HP-2-HMDI-R.T.-15 | | | | x | N.D. | N.D. | | | | |
| HAP-polyetherdiamine L-2000-R.T.-31 | - - - | N.D. | - - - | - - - | N.D. | N.D. | | x | | |
| HAP-polyetherdiamine L-2000-60°-32 | | x | | | 1.4xs | 0 | | | | x |

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TABLE 1 (Concluded)

| <u>Oxidizer-Fuel-°C-Days</u> | <u>Evolved Gases, Moles:100 Moles of Oxidizer</u> | | | | | | | | | |
|--|---|----------------|--------------|--------------|----------------------|----------------------|-----------------------|----------------|--------------|--------------|
| | <u>CO₂</u> | | | | <u>O₂</u> | <u>N₂</u> | <u>N₂O</u> | | | |
| | <u>0</u> | <u><0.1</u> | <u><1</u> | <u>>1</u> | | | <u>0</u> | <u><0.1</u> | <u><1</u> | <u>>1</u> |
| HAP-60°-(30 to 60) | | | | | | | | x | | |
| HAP-85°- <5 | | | | | | | | x | | |
| HAP-85°-(5,14) | | | | | | | | | x | |
| HAP-85°-49 | | x | | | 0.01 | 0.05 | | | | x |
| HP-2-60°-77 | | | | | 0.01 | 0.02 | | | | |
| HP-2-85°-(25 to 35) | | | | | | 0.20xs | | | | |
| HP-2-85°-76 | | | | | 0.08 | 0.8xs | | | | |
| HAP-ethylene glycol dimethyl ether- 85°-40 | | x | | | 0.10xs | 0.05 | | x | | |
| HP-2-ethylene glycol dimethyl ether- 85°-41 | x | | | | 0.20xs | 0.20 | | | | |

a/ xs indicates oxygen or nitrogen clearly in excess of air proportion.
b/ N.D. = no data available.

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(U)

Carbon dioxide evolved in 9 of the 34 experiments with HAP; 5 of the 9 were conducted at 35°C, and a sixth lasted 4 months at 60°C. Fifteen of the 26 experiments with HP-2 gave positive tests for carbon dioxide; 10 of the positive tests were at 60°C, 4 at 85°C, and 1 (hexane, 5 months) at ambient temperatures.

(U) One therefore concludes that HP-2 is capable of slow (0.1 to 1 CO₂: 100 HP-2 in 1 - 2 months) oxidation of these types of organic materials at 60°C, and may exhibit this potential over longer periods of time at ambient temperatures. With HAP, by comparison, 60° can be viewed as a threshold temperature -- the temperature at which oxidation becomes measurable only after 5 - 6 months. It should be emphasized that while the difference is there, HP-2 is much the same as HAP in general oxidizing ability. Both exhibit only slight oxidizing tendencies. HAP presently gets a slight nod over HP-2 for long-term ambient temperature compatibility with substances with which both are essentially compatible.

(C) HP-2 and HAP were very similar, in the oxidative sense, in their response to substances outside the essentially compatible group. Urethanes, isocyanates, and epoxides ordinarily reacted to about the same extent with HAP or with HP-2. The area of significant difference is the N-H containing materials. HP-2 was clearly more compatible than HAP with NIEB and MAPO. The superior compatibility of HP-2 is believed due to the fact that displacement of one of the two moles of perchloric acid can be effected with HP-2 without seriously affecting compatibility, while displacement of perchloric acid from HAP yields unstable and reactive hydroxylamine.

C. Nonoxidative Reactions of HAP and HP-2

(U) In this section we shall discuss observed reactions which would appear to be generally of greater significance to propellantry than is oxidation. The reactions are characteristic of organic systems in the presence of acids and dehydrating agents. These reactions are described in Table 2.

(C) 1. Ether rearrangement: The first evidence of rearrangement of ethers was obtained from Adiprene L-100, a derivative of polytetramethyleneoxide. In the presence of HAP or HP-2 at ambient temperatures, this "ether" readily evolves tetrahydrofuran. This behavior is most readily interpreted in terms of depolymerization, i.e., the lifting out of tetramethyleneoxide followed by cyclization to tetrahydrofuran.

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TABLE 2

(C) SPECIAL PHENOMENA

| <u>Organic Substance</u> | <u>Phenomenon</u> | <u>Remarks</u> |
|------------------------------|-----------------------------------|--|
| Butene-1 | Polymerization | Slowly by HAP at R.T., very slow by HP-2. |
| Butene-1 | Isomerization to trans-2-butene | By HP-2 after 125 days at R.T. |
| Certain ethers | Formation of ethylene | From ethyl ether plus HAP at 85°C-65 days, not at 60°-141 days. |
| | Formation of propylene | From 1,2-epoxy-3-isopropoxypropane plus HAP or HP-2 at R.T. and 60°C. |
| | Formation of propane | From HP-2 plus 1,2-epoxy-3-isopropoxypropane at R.T. and 60°C. |
| | Rearrangement | Tetrahydrofuran a major product from HAP or HP-2 plus Adiprene L-100 at R.T., after 5-10 days. |
| | | Diethyl ether a major product from HAP or HP-2 plus 1,4-diethoxybutane after 1-2 weeks at R.T. and 60°. With HP-2 at 60° ethanol was also observed. Other products were not identifiable by IR; tetrahydrofuran a likely second product. |
| | | Major products from HAP plus ethylene glycol dimethyl ether, after 2 months at 85°C, were dimethyl ether and ethyl acetate. |
| Polybutadiene derivatives | Formation of ethylene and methane | From: HAP-Telagen CT-R.T.-111 days. HP-2-Telagen CT-R.T.-111 days (methane, no ethylene). HAP-Telagen CT-60°-54 days. HP-2-R-45-M-60°-52 days. |

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TABLE 2 (Concluded)

| <u>Organic Substance</u> | <u>Phenomenon</u> | <u>Remarks</u> |
|------------------------------|---|--|
| Epoxides | Polymerization | A general phenomenon; HP-2 plus ethylene oxide spontaneous at R.T.; HAP plus ethylene oxide slow (weeks) at R.T.; liquid epoxides generally slow with both HAP and HP-2. ERL 0510 perhaps most resistant of commercial epoxides, but polymerizes in 2-3 months at R.T. |
| Urethanes | Evolution of CO ₂ | Slow, but universally observed at R.T. from oxidizer-urethane systems, including urethanes having molecular weights in 2000 range. Carbon dioxide evolution believed due (but not proved) to decarboxylation of urethane functionality. |
| Isocyanates | Evolution of CO ₂ | Isocyanate-oxide systems are most vigorous CO ₂ evolvera of systems tested; order of decreasing reactivity: hexamethylene diisocyanate > Adiprene L-100 > toluene diisocyanate. |
| Amines | Displacement of NH ₂ OH and N ₂ H ₄ | By polyether diamine L-2000. |
| Alcohols | Dehydration | To appropriate ether; specifically observed only with ethanol; HP-2 more effective than HAP. |

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(U) At 85°C, two reactions of interest were found. In the first, ethylene was generated from diethyl ether and HAP; no ethylene was found over HAP plus ether at 60°C, even after 141 days. In the second 85°C reaction, dimethyl ether and ethyl acetate were formed from HAP and ethylene glycol dimethyl ether. The dehydration of diethyl ether to ethylene is not unusual chemistry -- it is to be expected at elevated temperatures in the presence of acid. The dimethyl ether-ethyl acetate set of products from ethylene glycol dimethyl ether is somewhat unusual, especially since very little oxidative reaction occurred. Formally, these products can arise from ether cleavage accompanied by rearrangements as indicated below.



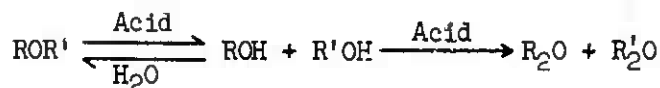
(C) The reactions at 85°C are of scientific interest, but bear little relationship to propellant stability unless they are indicative of reactions which may occur at lower temperatures. The generation of THF from Adiprene L-100 at ambient temperatures does indeed imply that HAP and HP-2 are capable of cleaving ether linkages under mild conditions. Adiprene L-100 hardly constitutes a fair test of this possibility, since it is both a urethane and an isocyanate -- both of which react in their own way with the oxidizers.

(U) In order to better test ether cleavage, a mixed ether, 1,4-diethoxybutane, was tested with HAP and HP-2. With diethoxybutane, tetrahydrofuran and diethyl ether were the expected products. First tests were conducted at ambient temperatures in the sidearms of infrared cells. No definite new substances were detected through infrared spectra of volatiles over HAP-diethoxybutane or HP-2-diethoxybutane. The volatiles were then pumped into another infrared cell. The resultant spectra showed ethanol plus a carbonyl compound from HP-2, and a carbonyl compound from HAP. The C-C-C functionality was present in both cases. Sealed tubes were employed in subsequent experiments at 60°C and at ambient temperatures. In all cases diethyl ether was a definite product, with tetrahydrofuran a possible second product. Reaction times were about 3 weeks.

(U) The results with 1,4-diethoxybutane show that ether cleavage does occur, at ambient temperatures, in the presence of HAP and HP-2. The cleavage is believed due to the acidic character of the oxidizers, possibly with an assist from trace water.

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(U) Another reactant, 1,2-epoxy-3-isopropoxy propane, gave somewhat different results, but results nevertheless generally consistent with results obtained with other ethers. Propylene was a usual product from this reactant plus HAP and HP-2. The propylene was barely detectable by infrared after 2 months at ambient temperatures. After 1-1/2 to 2 months at 60°C, larger quantities (estimated 1 C₃H₆:100 HAP or HP-2) were evolved. The epoxide polymerized to a viscous, dark liquid at both temperatures. The formation of propylene indicates ether cleavage and dehydration. Since epoxides are effective water scavengers, thus competing with the oxidizers for trace water, this behavior is not unexpected.

(C) 2. Dehydration of alcohols: Ethyl alcohol is dehydrated readily to diethyl ether by HP-2, slowly by HAP. No additional alcohols were tested except substances such as R45 M, a high molecular weight alcohol (M.W. = ca. 2100). We assume that dehydration is universal, but readily detectable only when by-product ethers are volatile.

(C) 3. Ethylene and methane from poly butadiene derivatives: Ethylene and methane evolved slowly from Telagen CT and R45 M in contact with HAP and HP-2. We have no explanation of this behavior.

(C) 4. Polymerization of epoxides: As mentioned previously, epoxides appear to be universally susceptible to polymerization in the presence of HAP or HP-2. Of interest is the observation that polymerization was usually more extensive at room temperature than at 60°C. It is possible that cleavage-rearrangement reactions occur at 60°C, and that molecular weights thus remain low.

(U) 5. Polymerization-isomerization of olefins: Butene-1 is the only tested simple olefin. This olefin polymerizes slowly in the presence of HAP. After 125 days in contact with HP-2, butene-1 was converted, apparently quantitatively, to trans-2-butene.

(U) Somewhat unexpectedly, butene was one of the difficultly oxidizable compounds. Ethylene and propylene were elevated temperature reaction products, and it thus is evident that aliphatic olefins are quite resistant to oxidation.

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(C) 6. Evolution of carbon dioxide from urethanes: As mentioned previously, it is our opinion that carbon dioxide arises from urethanes by decarboxylation rather than by oxidative reactions involving the ClO_4 group. Since this opinion or conclusion cannot be verified or denied by present data, no further comment is necessary.

D. Comparison with Ammonium Perchlorate

(C) Several experiments with ammonium perchlorate were conducted at 60°C for 3 months, and at 85° for 1-1/2 to 2 months. Tested substances (Table 3) were propane, ethanol, ethyl ether, ethyl acetate, ethyl-N-ethyl carbamate, and ethyl-N-ethyl carbanilide. Only the latter compound yielded evidence of reaction. The remainder, including ethyl-N-ethyl carbamate at 85° for 2 months, appeared to be completely compatible. Similarly, AP did not react at ambient temperatures over a 7-day period with hexamethylene diisocyanate, a substance which reacts extensively with HAP and HP-2 under the same conditions.

(C) It is apparent that AP is substantially more inert than HAP and HP-2. It is also apparent that more extensive comparisons are in order. We were so impressed with the complete lack of evidence of reaction with AP at 85°C , as compared to the fairly common observation of small quantities of (variously) carbon dioxide, N_2 , O_2 , and N_2O from HAP and HP-2 systems that more extensive comparisons were not initiated. We thus can state with confidence that AP is, as expected, the most stable and compatible of the three oxidizers. We need, however, a wider basis of comparison in terms of a greater variety of reactants and more severe time-temperature conditions.

E. Oxidizer Stability

(U) 1. The stability of HAP: Early studies showed that HAP evolved small quantities (less than 0.01 moles:100 moles HAP) of nitrogen and nitrous oxide in 1 - 2 months at 60°C , and that decomposition occurs fairly spontaneously at 85°C after an induction period of 10 - 14 days. The 60°C data were fairly scattered, and it was concluded that the observed quantities of decomposition products were typical of either an induction period or of degradation due to impurities. No further data were obtained. In several HAP-fuel experiments at 85°C , evidence of oxidizer decomposition was much less than that predicted from the study of HAP by itself. The data uniformly indicate HAP to be more stable at 85°C in the presence of fuels than in their absence.

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TABLE 3

(C) STUDIES OF AMMONIUM
PERCHLORATE

| <u>Fuel</u> | <u>Time, days</u> | <u>°C</u> | <u>Results</u> |
|-------------------------------|-------------------|-----------|--|
| Propane | 98 | 60 | No change |
| Ethanol | 98 | 60 | No change |
| Diethyl ether | 98 | 60 | No change |
| Ethyl acetate | 81 | 60 | No change |
| Propane | 50 | 85 | No change |
| Ethanol | 50 | 85 | No change |
| Diethyl ether | 50 | 85 | No change |
| Ethyl acetate | 45 | 85 | No change |
| $C_2H_5NHCOOC_2H_5$ | 59 | 85 | No change |
| $C_6H_5N(C_2H_5)COOC_2H_5$ | 38 | 85 | Reaction: mostly nitrogen, trace N_2O and CO_2 |
| Hexamethylene diisocyanate | 7 | R.T. | No change |
| Toluene diisocyanate | 7 | R.T. | No change |

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(U) Nitrous oxide was evolved in an unpredictable manner, generally more often than not, from HAP-fuel systems at 60°C and 85°C. A notable exception is the epoxides; nitrous oxide was not found, even at 60°C.

(U) Nitrogen and oxygen also evolved in a fairly unpredictable manner from HAP-fuel systems. One perhaps should say that nitrogen and oxygen were quite often found, but where they were present in proportions close to that of air, it was not possible to determine whether the origin was air or evolved nitrogen. For this reason, in Table 1, we have noted (with xs) instances in which either component was clearly present in proportions which indicated it to have been evolved from the sample. The epoxides again present a uniform, clear-cut case of oxygen evolution.

(U) 2. The stability of HP-2: We have found that HP-2 decomposes slowly at 85°C. In 25 - 35 days, approximately 0.2% decomposition has occurred as determined by nitrogen evolution. After 76 days the extent of decomposition was 0.8%. At 60°C, essentially no decomposition occurred in 77 days. Nitrogen is a common product in HP-2 fuel systems. As with HAP, however, oxygen was evolved uniformly from HP-2-epoxide systems.

F. Preliminary Studies of PBEP

(U) Screening studies have been conducted in glass infrared cells. The PBEP, or PBEP plus HAP, HP-2 or AP, was placed in a sidearm attached to the cell, and volatile products were monitored by infrared. The results are collected in Table 4.

(C) The PBEP as received was diluted with methylene chloride. This solution was charged to the infrared cell, and methylene chloride was removed by evacuation at room temperature. Methylene chloride always evolved slowly into the gas phase, however. Pertinent observations are as follows:

(C) 1. In glass, PBEP slowly generated SiF_4 and HCN over a 6-week period. In addition, traces of acetone plus a volatile hydrocarbon evolved; these presumably are residual from process treatments.

(C) 2. At 85°C, SiF_4 and HCN evolved more rapidly (hours), and HNF_2 (one band at 900 cm^{-1}) was also observed.

(C) 3. PBEP-HAP and PBEP-HP-2 systems evolved SiF_4 , HCN and HNF_2 at ambient temperatures. Quantities of SiF_4 and HCN were 3 - 4 times the quantities observed over PBEP alone. Nitrous oxide evolved from PBEP plus HAP.

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TABLE 4

(C) STUDIES OF PBEP

| <u>System</u> | <u>Observations</u> |
|---|---|
| PBEP, R.T., 1. glass IR cell | Residual CH_2Cl_2 ; slow formation of SiF_4 and HCN; trace of volatile organic consisting of acetone (process solvent?) and a volatile hydrocarbon. Quantities of SiF_4 and HCN are approximately 1 mole per 100 monomer units after six weeks. |
| PBEP, 85°, in glass IR cell | SiF_4 and HCN evolved; quantities in 2 hours greater than after six weeks at R.T. Difluoramine observed, band at 900 cm^{-1} . |
| PBEP-HP-2 or HAP, in glass IR cell, R.T. | SiF_4 , HCN and HNF_2 . Quantities of SiF_4 and HCN three to four times the quantities observed over PBEP alone. N_2O evolved from PBEP-HAP. |
| PBEP-AP, R.T., in glass IR cell | Barely detectable SiF_4 in two weeks. |

(C) 4. Ammonium perchlorate-PBEP is the most stable system tested. Silicon tetrafluoride, the only observed volatile product, was barely detectable in two weeks.

(C) These results may be misleading in that the experiments were conducted in glass, and the glass may have contributed to the observed instability. One concludes as a minimum that this particular sample of PBEP is glass reactive; whether the glass reactivity arises from PBEP plus glass or HF plus glass remains unknown. One tentatively concludes that HNF_2 evolves from PBEP at 85°C, though here again glass may have played an important role. There seems to be little reason to question the conclusion that contact of PBEP with HAP or HP-2 accelerates decomposition. Furthermore, PBEP apparently facilitates the decomposition of HAP, as evidenced by N_2O evolution. The latter results contrast sharply with the behavior of ammonium perchlorate, which exhibited a stabilizing effect on PBEP.

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G. EPR Studies

(U) Electron paramagnetic resonance (EPR) spectra have been monitored over several months time on HAP, HP-2, and AP to determine if any radical species are generated during the reactions of these compounds with organic materials. The results have shown that radical generation is small or nonexistent. Even systems which turn "black" during reaction give only weak broad signals which have no distinguishing characteristics to facilitate their identification.

(C) Systems which have been studied include HAP in a complete UTC system, AP in a complete UTC system, HP-2 as received from Thiokol, HP-2 crude prepared at MRI, HP-2 prepared and dried at MRI, HAP + TDI, HP-2 + TDI, AP + TDI, HAP + HMDI, AP + HMDI, HP-2 + ethyl ether, AP + ethyl ether, AP + ethyl alcohol, HP-2 + ethyl alcohol, HAP + ERL 0510, and ERL 0510 by itself. The discussion will be broken down into these various systems.

(C) 1. UTC systems: HAP in a UTC binder (NTEB, UTREZ, MRPX) gave very weak broad signals after standing 90 days at room temperature. After 140 days, these signals disappeared. The same system held at 60°C did not give a signal until 120 days. This signal was somewhat stronger than the signal from the room temperature sample. After 130 days, the 60°C sample had lost much of its EPR signal, although the signal persisted detectably to 160 days.

(U) AP in the UTC binder gave weak signals shortly after preparation. This signal persisted for about 140 days. When the sample was held at 60°, the same EPR signal developed only with reduced intensity. As was the case with the HAP sample at 60°, the heated AP sample gave a signal which persisted for a longer period, disappearing completely after about 170 days.

(C) 2. HP-2: Several samples of HP-2 in various stages of purity were monitored with EPR. These samples include HP-2 received from Thiokol, HP-2 crude as prepared at MRI, and dried HP-2 purified from the crude material. The results of the EPR studies are as follows.

(C) The Thiokol HP-2 at room temperature gave no EPR signal during 100 days of monitoring. The same sample held at 60° immediately gave weak broad signals which increased in intensity for about 35 days, then decreased and disappeared entirely after about 60 days. This signal in the heated sample is believed due to reaction between the HP-2 and tricresylphosphate (TCP) residue not removed from the HP-2. (The HP-2 supplied by Thiokol is diluted with TCP which must be removed by sieving. Our analysis of the sieved product showed some residual TCP.) Because of the apparent reaction between HP-2 and TCP at elevated temperatures, we decided to use "dried" HP-2 as prepared at MRI.

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(U) The dried HP-2 prepared at MRI gave the usual weak broad undefined signals for about 50 days after preparation. If held at 60°, this signal did not appear until 30 days; however, it too disappeared at 50 days.

(U) The crude HP-2 at room temperature did not give the signal until about 40 days. This signal disappeared after 55 days. The 60° sample gave weak signals after 8 days, which persisted to 55 days, disappeared and then weakly reappeared at 85 days and finally disappeared a second time after 100 days.

(C) None of the signals generated in the MRI-prepared samples were of great intensity as compared to signals generated in the heated Thiokol HP-2 sample. The spectra do indicate, however, some changes in the HP-2 standing alone in an evacuated tube.

(C) 3. Oxidizer-isocyanate systems: HAP, HP-2, and AP were mixed with toluene diisocyanate (TDI) and hexamethylene diisocyanate (HMDI). The results of EPR monitoring are as follows:

(U) a. HAP + TDI (room temperature): A weak signal was detected after one day in the system, which had turned black. This signal increased in intensity until about 45 to 50 days when it suddenly disappeared. This signal did not reappear after 100 days standing.

(U) b. HP-2 + TDI (room temperature): This sample did not develop an EPR signal after standing 70 days.

(U) c. AP + TDI (room temperature): This sample did not develop a signal after standing 100 days.

(U) d. HAP + HMDI (room temperature): This sample did not develop a signal in four days. It was discarded at this time since earlier studies indicated excessive pressure buildup.

(U) e. AP + HMDI (room temperature): No signal was observed in the sample during 100 days of monitoring.

(U) 4. Oxidizer with alcohols and ethers: HAP, HP-2, and AP were mixed with diethyl ether and ethyl alcohol. No EPR signals developed after standing at room temperature and 60° for 100 days.

(U) 5. HAP + ERL 0510: Perhaps the most unexpected result of the EPR work was the appearance of signals in HAP-ERL 0510 systems. This system gave EPR signals parallel with those observed in the HAP-TDI systems. A fairly strong, sharp signal developed almost immediately after preparation

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and persisted for about 45 days. After this period, the signal intensity diminished considerably. Unlike the HAP-TDI system, the signal never completely disappeared and was still present after 100 days. The signal definitely came from reaction, since ERL 0510 studied separately never gave a hint of an EPR signal.

(C) The lack of interpretable data from the EPR studies is quite disappointing. This disappointment is especially true after its success in monitoring reactions between NP and various organics. However, careful consideration of the differences between the NP systems and the HAP, HP-2, and AP systems has led us to the conclusion that the ClO_2 radical molecule, so abundant in the NP systems, is not generated in the ammonium systems. The reason for this lack of ClO_2 can be traced to the oxidation state of the nitrogen nucleus in the cation.

(C) With NP, the nitrogen cation in NO_2^+ is in its highest oxidation state of +5. It cannot be oxidized any higher. Therefore, decomposition of the perchlorate to ClO_2 is possible. ClO_2 is a good oxidizing agent and will react with available materials and be reduced to Cl_2 or Cl^- ion, neither of which is paramagnetic. In the cases of HAP, HP-2, or AP, the oxidation states of the nitrogen atoms in the cation are -1, -2, and -3, respectively. Therefore, the nitrogen is capable of being oxidized to a higher oxidation state, and since paramagnetic decomposition products of the ClO_4^- anion are all oxidizing agents, no chlorine containing free radicals should be expected. If these radicals are generated at all, they would be immediately reacted out of the system by the reducing cation.

(C) This model is further substantiated by the observation that NOClO_4 did not give rise to ClO_2 signals as did NP. Since the NO^+ cation can be oxidized, it will be by the action of ClO_2 arising from the decomposition of the perchlorate ion.

(C) We can say, then, with confidence that the weak broad undefined signals in the HAP, HP-2, and AP systems are not due to any chlorine containing radical generated from the decomposition of the perchlorate ion. They must be due to either the cation or radicals in the organic matrix. However, they cannot be identified or followed with any accuracy because of their extreme breadth. The following is a discussion of our views on this phenomenon.

(U) EPR techniques can be used to study surface chemistry, since many unpaired electrons can be trapped on surfaces. In fact, one of the principal standards for calibrating EPR spectra is standard "pitch" prepared by diluting charred sugars in KCl. Piette (Ref. 12) has described the EPR spectra of a carbon black sample under various atmospheric conditions.

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If the sample is evacuated, the signal is sharp and well defined. If, however, air, or more significantly oxygen, is admitted to the sample, the EPR signal immediately becomes broad and ill-defined. More importantly, the total intensity of the signal does not change. Hence, radicals are not "scavenged"; rather they are "smeared" into a configuration which makes their EPR signal appear much weaker than it really is. The intensity of the signal lies in its broadness.

(U) The reason for the broadness of the signals in the HAP and HP-2 samples (of the order of 200 gauss) may be that oxygen is liberated as a product of reaction. This oxygen can then be retained in the system so that it can "smear" radicals into giving broad unresolved EPR signals which cannot be analyzed with any degree of authority.

H. NMR Studies

(C) Nuclear magnetic resonance (NMR) techniques have been employed to study changes in the proton resonances due to chemical reaction between HAP and organics. The studies have been broken down into two phases. Phase I has consisted of HAP by itself and in simple solvent systems including water, ethanol, and diethyl ether. Phase II has consisted of HAP in contact with organic "model" compounds (ethyl N-ethyl carbamate, ethyl N-ethyl carbanilide, 1,4-diethoxybutane, and 1,2-epoxy-3-isopropoxypropane) in chloroform solution. This latter phase was initiated in the final stages of the program to determine the extent of HAP's reaction with polymers.

(C) The results of Phase I are summarized in Table 5. In solution, HAP appears to have only one proton signal due to exchange among the NH protons and the OH proton in NH_3OH^+ . Both proton signals can be resolved in pure molten HAP. The presence of "acid" protons in combination with HAP (as seen by the H_2O and EtOH samples) tends to shift the HAP signal to higher magnetic field. Reaction of HAP with EtOH can be readily followed with NMR by watching the disappearance of the -OH group as a function of time. This reaction has been characterized as the dehydration of ethanol.



In all cases, the HAP appears to have been structurally changed after about 80 days as seen by broadening of the proton signals from the NH_3OH^+ cation.

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TABLE 5

(C) NMR SHIFTS OF HAP IN SIMPLE SOLVENT SYSTEMS*

| <u>Sample</u> | <u>Shift (ppm)</u> |
|--|--|
| HAP (molten at 100°C) | 9.71 NH_3OH^+ 7.45 NH_3OH^+ 6.44 (VW) HAP + H_2O |
| HAP + H_2O (1:1 molar ratio) | 6.28 |
| HAP (in Et_2O solution) | 7.88 |
| HAP + H_2O (1:1 molar ratio in Et_2O) | 6.00 |
| HAP + EtOAc (1:1 molar ratio in Et_2O) | 7.98 |
| HAP + EtOH (1:1 molar ratio in Et_2O) | 7.65 6.18 (doublet -- OH in EtOH -- disappears in 70-80 days) |
| HAP (in EtOH solution) | 4.08 |
| H_2O | 3.53 |

* Downfield in ppm from external cyclohexane reference.

(C) When the principal studies of HAP and organics revealed that reactions were primarily due to acid catalyzed reactions rather than oxidative reactions, Phase II of the NMR studies was initiated as an adjunct to the primary studies. The first study was with a HAP-urethane mixture suspended in MRPX. The urethane was made from phenyl isocyanate and a polybutadieneol (R45 M). The reaction was monitored for about 40 days using a Varian C-1024 Time Averaging Computer to look at the small quantities of urethane linkages in the system. Results showed no difference between the HAP sample and the pure urethane sample. It was then suspected that the urethane linkages were too few to observe meaningful changes in the total system. Therefore, we decided to look at "model" compounds with only specific functionalities

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which should react in the system. These model compounds were ethyl N-ethylcarbamate, ethyl N-ethylcarbanilide, 1,4-diethoxybutane, and 1,2-epoxy-3-isopropoxypropane. Of these four compounds, only 1,2-epoxy-3-isopropoxypropane showed any change in the presence of HAP. The change occurred in the first day of reaction. This reaction indicated polymerization of the organic and was characterized by a broadening and coalescence of sharp peaks typical of a polymerization type of reaction.

(U) With this one exception, no change in the NMR spectra of the organics was detected in about 80 days of reaction. Indeed, no change in the polymer formed from 1,2-epoxy-3-isopropoxypropane was detected in this period. The reason for this lack of change is believed due to the inherent sensitivity limitations of the NMR technique. If reaction occurs only to an extent of about 1%, the NMR does not have sufficient sensitivity to detect the change.

(U) Thus, on the basis of our NMR studies, we conclude that the reaction of HAP with organics proceeds to a fairly small extent, in the order of 1% or less. In long-term studies (several hundred days), the NMR spectra would probably show changes as reaction progresses.

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III.

SUMMARY AND CONCLUSIONS

(C) The results obtained in this program do not, as they stand alone, furnish the basis for passing judgment on HAP and HP-2. They do present a reasonably good picture of the reactivity and compatibility of the oxidizers with fuels in general, but this picture does not include compatibility in polymeric binder systems. Reaction rates are likely to be different, very likely slower, in cured polymer systems.

(U) Conclusions drawn from the results are as follows:

(U) 1. As expected, AP is more inert than HAP and HP-2.

(U) 2. Neither HAP nor HP-2 are vigorous oxidizing agents. The reverse is in fact true -- both exhibit but a relatively slight tendency to oxidize organic substances. HAP gets a slight nod over HP-2 in this respect.

(C) The simple, relatively nonfunctional organic substances begin to be susceptible, over 2- to 5-month periods, to oxidation by HAP at 60°C. At 60°C HP-2 fairly uniformly oxidizes the same class of compounds, though still slightly over 2- to 3-month periods. Very limited data indicate that substances such as hexane might be on the threshold of oxidation by HP-2 after 5 - 6 months at ambient temperatures, while no such evidence was obtained for HAP. HAP thus may be the more stable oxidizer for the long haul.

(C) 3. A variety of nonoxidative organic reactions are promoted by both HAP and HP-2. These generally are those expected in acid, dehydrating media. Typical reactions are rearrangement of ethers, dehydration of ethers and alcohols, polymerization of epoxides and olefins, rearrangement of olefins, alcohol condensation (limited evidence), decarboxylation, and displacement of hydroxylamine or hydrazine by strong bases. These types of reaction are in our opinion of greater significance than are the latent oxidizing abilities of HAP and HP-2. One thus expects HP-2 or HAP to slowly scavenge water from the organic substrate, even if this means creation of a carbon-carbon double bond and cleavage of carbon-oxygen bonds. Ether linkages are indicated to be subject to cleavage and rearrangement. Residual olefinic linkages are subject to slow rearrangement.

(C) These types of reactions are capable in theory of being the source of difficulty during curing processes, and during storage. Cure reactions thus may be less specific than desired, and extraneous undesired reactions

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are possible during the time interval in which the system is relatively fluid. After cure, a gradual alteration of polymer properties may result from rearrangements of structure.

(U) 4. We conclude, without experimental justification, that residual water may be important in the sense that it can aid and abet the oxidizers promote the type of reactions discussed in (3).

(C) 5. The urethane functionality is, we conclude, subject to slow decarboxylation by HAP and HP-2. Solid urethanes have not been tested, so we cannot assess the practical consequences of this property in a cured propellant grain. Points of urethane-oxidizer contact should be inherently reactive, but reaction rates may be negligibly slow.

(C) 6. Commercial epoxides polymerize in the presence of HAP and HP-2, and are slowly oxidized. The reaction rates are slow relative to usual cure times, and selection of an epoxide should be based on cure effectiveness and binder properties rather than on the basis of reactivity with the oxidizers.

(C) 7. Organic isocyanates are fairly reactive with both HAP and HP-2. Hexamethylene diisocyanate is in our opinion reactive enough to give trouble during cure reactions. Aromatic isocyanates (TDI) appear to react at an acceptably slow rate.

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APPENDIX

(C) GLOSSARY OF TERMS

| | |
|----------|---|
| HAP | Hydroxylammonium perchlorate; Thiokol Chemical Company, Elkton, Maryland; 97% pure by titration for weak acid. |
| HP-2 | Hydrazinium diperchlorate; Thiokol Chemical Company, Brigham City, Utah; 89.1% HP-2, 5.7% $N_2H_5ClO_4$, 5.2% unknown. |
| CY 175 | Alicyclic diepoxy acetate; Ciba Producta Company. |
| DER 732 | Polyglycol diepoxide; Dow Chemical Company. |
| DER 736 | Polyglycol diepoxide; Dow Chemical Company. |
| ERL 0510 | Trifunctional epoxide, base <u>p</u> -aminophenol; Union Carbide Corporation. |
| ERL 4221 | Alicyclic diepoxy acetate; Union Carbide Corporation. |
| UTREZ | Carboxy terminated polyisopropylene; United Technology Center. |
| NIEB | Nitrilotriethyl- β -ethyleneiminobutyrate; American Cyanamid Company. |
| MAPO | Trifunctional imine; R_3PO ; Interchemical Corporation. |
| TDI | Toluene diisocyanate. |
| CS-15 | Hydroxyl terminated polybutadiene, Sinclair Petrochemicals, Inc. |
| MAPS | Trifunctional imine; Interchemical Corporation. |
| HMDI | Hexamethylene diisocyanate; J. T. Baker Chemical Company. |
| MRPX | Isoparaffinic mineral oil; Shell Development Company. |
| PBEP | Poly-bis-difluoroaminopropylene oxide; Shell Development Company. |
| L-2000 | Amine-terminated polyether; Union Carbide Corporation. |

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|-------------------|---|
| Telgen CT | Carboxyl-terminated polybutadiene; General Tire and Rubber Company. |
| R-45-M | Hydroxyl-terminated polybutadiene; Sinclair Petrochemicals, Inc. |
| Adiprene L-100 | Urethane derived from polytetramethylene oxide and TDI; E. I. du Pont de Nemours and Company. |

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| | ROLE | WT | ROLE | WT | ROLE | WT |
| HAP HP-2 Hydroxylammonium Perchlorate Hydrazinium Diperchlorate PREP Compatibility Stability Reaction Mechanisms Oxidizer-Fuel Reactions | | | | | | |

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